

The THEORY of
ORGANIC CHEMISTRY

An Advanced Course

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PREFACE

THE STRUCTURAL THEORY of Kekule has been the growth hormone of organic chemistry. This theory used the atom and the bond as its fundamental concepts. It assumed no knowledge of either the composition of the atom or the nature of the bond. In recent years, however, modern theories of atoms and bonds have nearly filled these lacunae.

The deduction of the contents of organic chemistry from first principles with the aid of quantum mechanics is a goal to be reached; not an actual attainment. A simpler procedure is to incorporate G. N. Lewis' ideas of atoms and bonds with the classical structural theory. The result of this alliance is a structural theory whose fundamental concepts are valence electrons and atomic kernels. This electronic structural theory, and its application to organic chemistry, is the subject matter of this book.

We believe that a chemist can attain a fruitful knowledge of electronic structural theory without the ability to perform quantum mechanical calculations. However, quantum mechanics has contributed greatly to the development of the electronic structural theory. We have, therefore, included some digressions into quantum mechanics—notably in considering such fundamental concepts as the shared electron bond and molecular resonance.

We have attempted to keep a uniform point of view throughout rather than to produce a collection and evaluation of the mass of existing theories. This policy necessitates giving our opinions undue prominence. Ideas have been ignored on the slight grounds that we do not agree with them. Controversial points have been left without any decision because we have not reached one. Nevertheless we believe our policy to be the correct one in dealing with so live a subject.

The language of the new theories of organic chemistry has not had time to become uniform. The same ideas are expressed in different words by different authorities. C. K. Ingold, whose contributions to electronic structural theory are second to none, has developed a language to express his ideas. We have given scant recognition to this language, and have even taken certain liberties with it.

Actually we are in very close agreement with Professor Ingold's theories.

In the course of the preparation of the manuscript, we have had occasion to refer frequently to a number of very useful existing texts, chief among which are Gilman's *Organic Chemistry*, Watson's *Modern Theories of Organic Chemistry*, Pauling's *The Nature of the Chemical Bond*, and Freudenberg's *Stereochemie*. Special thanks are due to Professor Pauling for the original of Figure 9.

It is indeed a pleasure to acknowledge the co-operation of our colleagues, Professor Gilbert N. Lewis, Professor K. S. Pitzer, Dr. R. S. Halford, and Dr. David Lipkin, in the reading and discussion of manuscript and proof; and of Mrs. Gerald Branch, to whose patience and understanding this book owes its existence.

G. E. K. B.
M. C.

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CHAPTER I

THE DEVELOPMENT OF STRUCTURAL CHEMISTRY

1. VALENCE

A molecular formula of a substance is obtained from its molecular weight and a determination of the proportions of the elements present. It is found that compounds corresponding to all conceivable empirical formulas cannot be prepared. This restriction is explained by assuming that only a certain integral number of combinations is possible for each kind of atom. The number of combinations of an atom in a molecule is called its valence in that molecule. Valences are associated not only with atoms but also with elements. A valence is assigned to an element when it is found that the atoms of that element are often found with the given valence. An element may be found to have a single valence or a limited set of valences. This number or set of numbers associated with an element is a valence rule. The valence rules for a set of elements restrict the preparable compounds of these elements to those with molecular formulas in which the valence rules are obeyed.

The valence rules recognize that on heating to a sufficiently high temperature all compounds eventually dissociate and that in the resulting fragments anomalous valences must exist. The rules are applicable only to compounds that can be obtained at ordinary temperatures and concentrations. Further, an attempt is made to distinguish between chemical and physical cohesion, only the former being subject to valence rules. Thus in liquid hydrogen there must be many atoms combined to each atom, but only one of these combinations is sufficiently strong to be considered as chemical and resulting from the valence. Further, we find occasional exceptions to valence rules unless they are made so broad as to be useless. Thus in nitric oxide the nitrogen is divalent, but as this valence is so rare for nitrogen atoms, two is not included among the valences of nitrogen, and nitric oxide is considered as an exceptional compound.

It is not feasible to identify the valence of an atom in a compound with the number of other atoms with which it is combined, for an atom may combine with another by more than one valence. Thus